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13. ABSTRACT (Maximum 200 words)

The purpose of this project was to facilitate technology transfer between the Center for Multiphase Research (CMR) and the Waterways Experimental Station (WES). The research areas of interest and specific tasks were:

Model Formulation: provide WES with the latest research on the development of a thermodynamically rigorous model formulation for multiphase flow.

Split-Operator Methods: demonstrate a split-operator numerical method on a problem of interest to WES (i.e., sorption and degradation of explosives in saturated groundwater systems).

Sorption-Desorption Relations: model the fate and transport of explosives subject to sorption and degradation using data provided by WES.

Advanced Oxidation Processes: demonstrate and provide a numerical model capable of modeling ex situ peroxone processes.

The objectives of the project were met through a series a seminars, the transfer of computer codes, and a technical document.

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Final Report

Technology Transfer of Basic Research on Multiphase Subsurface Fate and Transport

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1 March 1998 - 14 January 1999

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February 21, 2000

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Introduction

A University Research Initiative (URI) grant to investigate flow and transport phenomena in multiphase systems was made to the Departmental of Environmental Sciences and Engineering at the University of North Carolina in July of 1992. Because the URI grant funded a substantial amount of research in an area with a significant number of applications, an opportunity existed for significant technology transfer. Discussions between personnel at the Center for Multiphase Research (CMR) and the Waterways Experimental Station (WES) led to the selection of a few research areas where results from the CMR could be applied to environmental problems of interest to WES. The research areas of interest to WES and objectives for this project were:

Model Formulation: provide WES with the latest research on the development of a thermodynamically rigorous model formulation for multiphase flow.

Split-Operator Methods: demonstrate a split-operator numerical method on a problem of interest to WES (i.e., sorption and degradation of explosives in saturated groundwater systems).

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Advanced Oxidation Processes: demonstrate and provide a numerical model capable of modeling ex situ peroxone processes.

Summary

Model Formulation

A seminar was presented at WES to explain evolving work in the area of model formulation. The key issue is that existing models are built upon ad hoc extensions to Darcy's law and have many shortcomings, and are in general unsatisfying. For example, the traditional model does not account for the dynamics between capillary pressure and saturation, makes no specific account for the role of interfaces between phases, does not account for transfer of momentum across interfaces, and requires hysteretic relations among capillary pressures, saturations, and interfacial areas. The seminar touched on an evolving, rigorous approach in which microscale equations were averaged to the macroscale and closed with thermodynamically constrained constitutive relations, which may be fully specified using pore-scale modeling techniques. The use of pore network modeling and lattice Boltzmann modeling approaches for this purpose was discussed.

Split-Operator Methods

Many of the environmental problems of interest to WES include advective and dispersive transport and reaction processes. Mathematical models for simulating environmental processes that include mass transfer, nonlinear reactions, multiple species, and multiple dimensions can require significant computational effort. Split-operator (SO) numerical methods can be used to significantly reduce the computational demands of simulating some of these problems. . We demonstrated an iterative split-operator numerical method on a model for sorption and degradation processes. Briefly, the ISO algorithm is given by: (1) solving the transport portion of the problem over a full time interval, assuming the reaction and mass transfer contributions are known; (2) solving the reaction and mass transfer portion of the problem over a full time interval, assuming the transport contributions are known; and (3) iterating over the first two steps in the algorithm until a convergence criterion is satisfied. The model was used to interpret trinitrotoluene (TNT) sorption and degradation in batch and column experiments. WES provided the experimental data. The details of the numerical methods and modeling results were presented in a seminar at WES. We also provided WES with a computer code that implements a variety of SO methods.

Sorption-Desorption Relations

Data from batch and column experiments on the sorption and degradation of TNT was provided by WES (*Natural Attenuation of Explosives in Soil and Water Systems at DoD Sites: Interim Report*, 1998, Technical Report EL-98-, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS). We modeled the behavior of TNT in a silty sand and lean clay. Rate-limited sorption in the batch and column experiments was modeled using a two-site approach (i.e., instantaneous equilibrium sites and rate-limited sites described by first-order mass-transfer). Degradation was modeled as a first-order reaction. Sorption equilibrium and rate model parameters were estimated from the data. Degradation rates were estimated assuming steady state conditions in the column experiments.

The experimental and modeling results for the column experiments are shown in Figures 1 and 2. The modeling results are in good agreement with the data for the sorption phase of both experiments. The model does not accurately simulate the desorption phase of the CL lean clay experiment. The modeling results indicate that TNT sorption was rapid, with the majority of the sorption being associated with the instantaneous equilibrium sites. Analysis of the steady-state breakthrough curves indicted TNT half lives of 348 and 276 days for the SM silty sand and CL lean clay, respectively.

The results of the TNT modeling and an update of current rate-limited sorption models were presented in a seminar at WES.

Advanced Oxidation Processes
Ex situ advanced oxidation processes can be used for treating a variety of organic contaminants (e.g., TCE, PCE, TNT, RDX, and atrazine) of interest to WES. We developed a model for simulating advanced oxidation processes in batch and column systems. The model accounts for the fate and transport of multiple species in an aqueous phase and a gas phase subject to multiple reactions and mass transfer between the phases. In a seminar at WES, we described the theory behind the model and demonstrated the model's utility by using the model to simulate a peroxone oxidation process similar to that used for the destruction of explosives. We also provided WES with the latest version of the model and sample data sets.

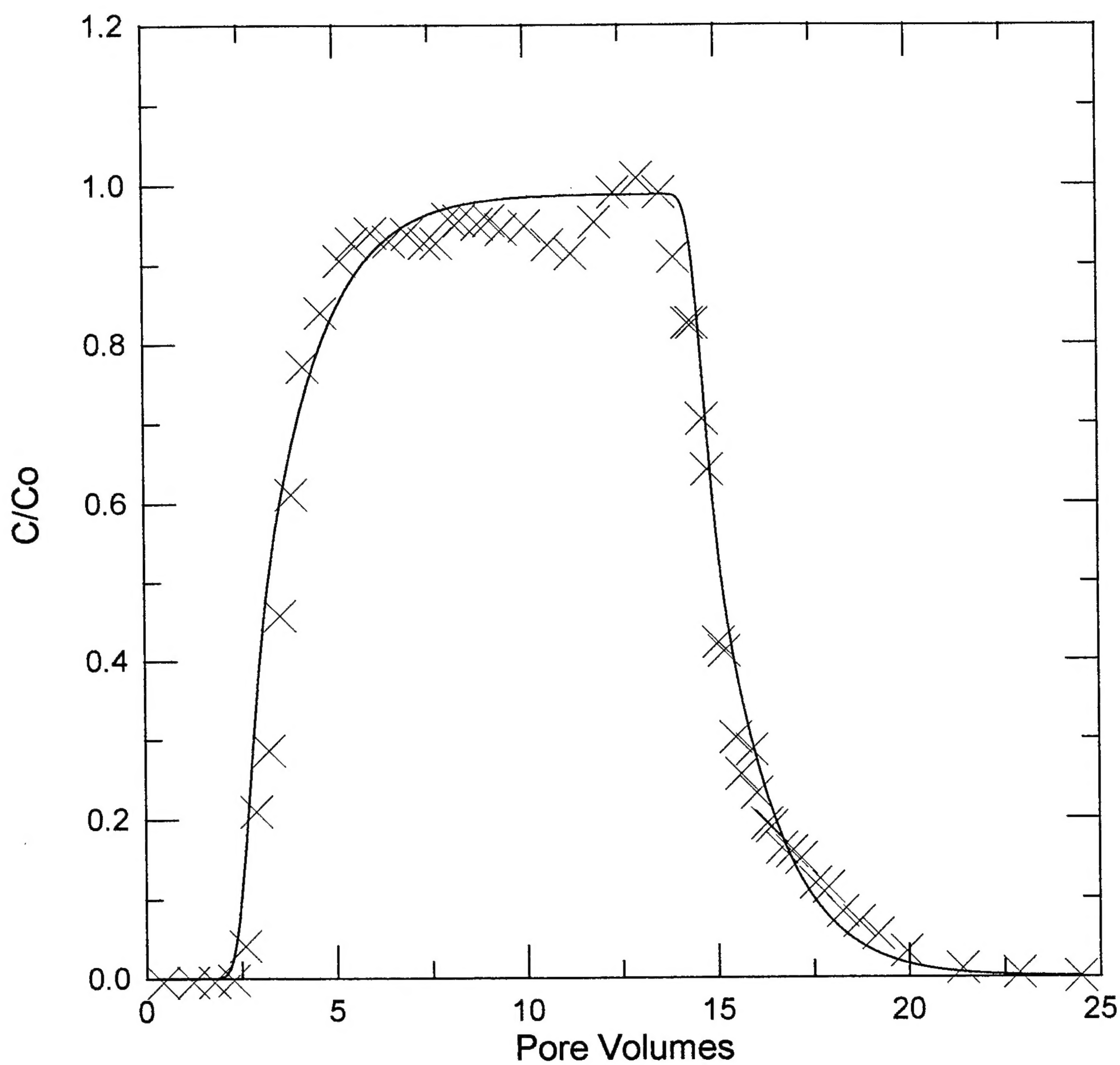

Figure 1. Column study and model fit for TNT on SM silty sand.

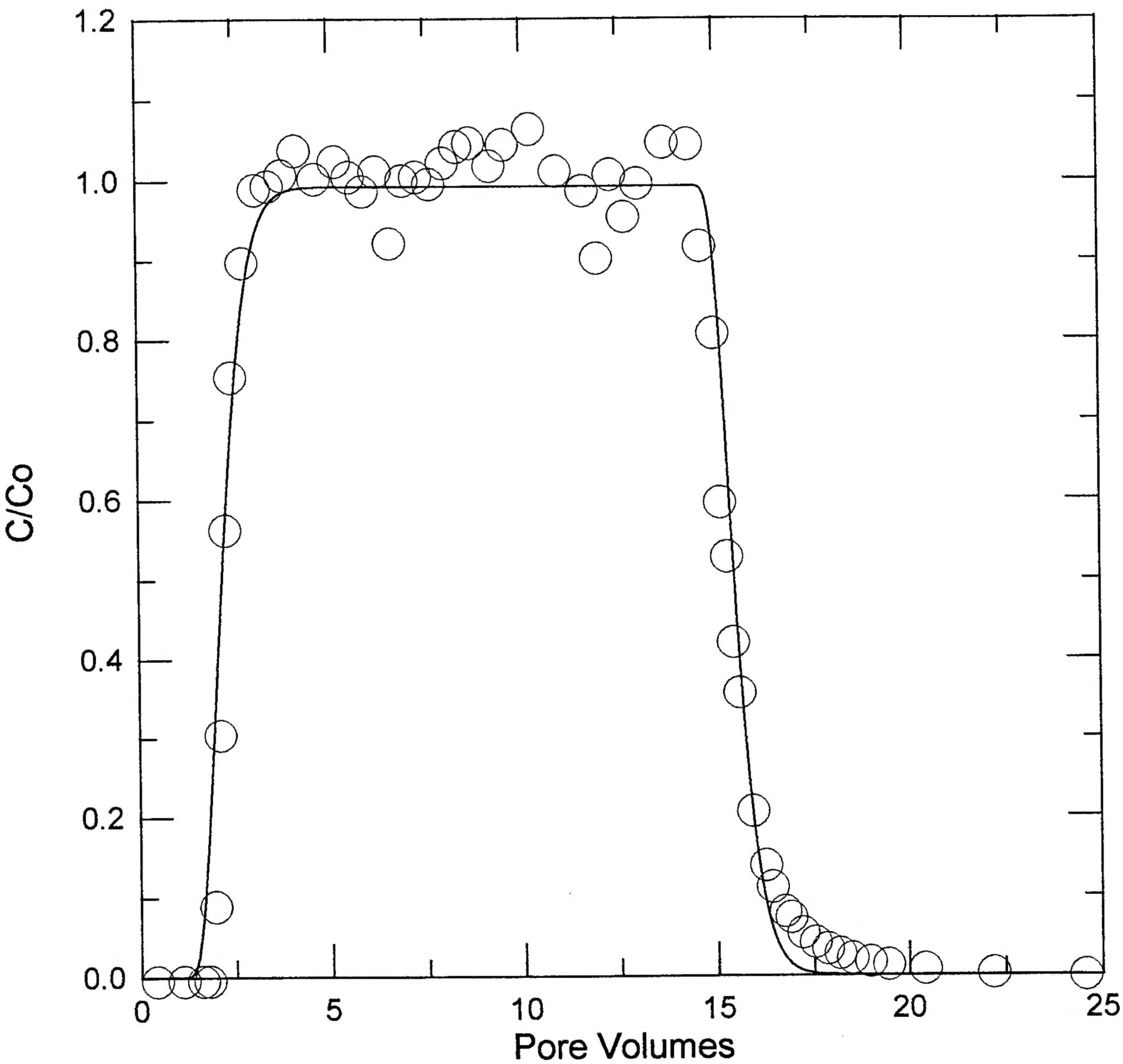

Figure 2. Column study and model fit for TNT on CL lean clay.

Publications and Technical Reports

Technical Reports

Pedit, J. A. and C. T. Miller, Demonstration of a Split-Operator Numerical Method for Modeling Sorption and Degradation Processes, Technical Report for Contract/Grant Number: DAAG55-98-1-0221, 21 February 2000, 15 pages.

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Inventions

None

Bibliography

None

Appendixes

None